(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開2001－64004
（Ｐ2001－64004Ａ）
(43)公開日　平成13年３月13日（2001.3.13）

| (51)Int.Cl.⁷ | 識別記号 | ＦＩ | ﾃｰﾏｺｰﾄﾞ(参考) |
|---|---|---|---|
| Ｃ０１Ｂ　31/02 | １０１ | Ｃ０１Ｂ　31/02 | １０１Ｆ　４Ｇ０４６ |

審査請求　未請求　請求項の数９　ＦＤ　（全８頁）

(21)出願番号　特願平10－225471

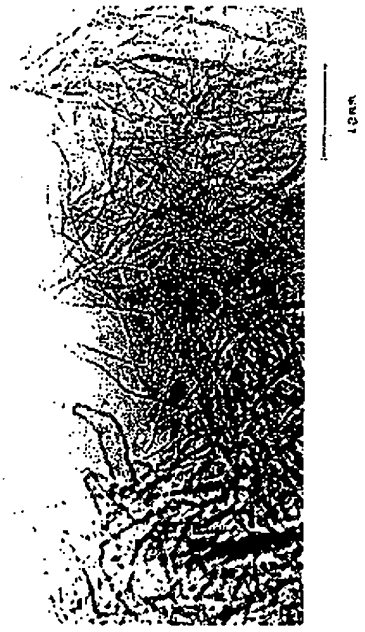
(22)出願日　平成10年７月25日（1998.7.25）

(71)出願人　396020800
科学技術振興事業団
埼玉県川口市本町４丁目１番８号
(71)出願人　598107426
センター　サントル　ナショナル　ド　ラ　ルシェルシュ　シアンティフィックス
フランス　75794　パリス　セデックス　16　ミシェル　アンジュ　3
(71)出願人　598107437
飯島　澄男
千葉県我孫子市並木７－３－28－Ａ301
(74)代理人　100093230
弁理士　西澤　利夫

最終頁に続く

(54)【発明の名称】　単層カーボンナノホーン構造体とその製造方法

(57)【要約】
【課題】　ナノ黒鉛構造の新しい物質とその製造方法を提供する。
【解決手段】　炭素原子の大きさに相当する厚みの単層で中空円錐形状の構造を持つ単層カーボンナノホーン構造体とする。



* NOTICES *



1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]
[0001]
[Field of the Invention] Invention of this application relates to the monolayer carbon nano horn structure and its manufacture approach. It is related with the still more detailed monolayer carbon [ which has the new fine structure of a nano meter scale with invention of this application useful to expansion of new functionality material ] nano horn structure, and its manufacture approach.
[0002]
[Description of the Prior Art] In recent years, the carbon matter which has the fine structure of a nano meter scale attracts attention as a monolayer or a multilayer carbon nanotube, fullerene, a nano capsule, etc. The application to an electronic ingredient with these carbon matter new as nano structure graphite (graphite) matter, a catalyst, an optical ingredient, etc. is expected.
[0003] About the carbon nanotube of these, even if the achievements by the artificer of this application are accepted, it is. And about the nano structure graphite matter known conventionally, even if it was required that it should have been manufactured by the carbon arc electric discharge method or the carbonaceous laser evaporation method, and to carry out simultaneous evaporation of a metal like Fe, nickel, and Co as a catalyst should have been made into a generation condition in these manufacture approaches, and conditions, such as temperature for generation, should have been chosen strictly, it was required.
[0004] However, about the nano structure graphite matter, since future technical development is expected, it is in the situation that the further energetic examination about the relation between the unique retrieval about the nano-scale fine structure itself, and a generation method, conditions and structure is called for. For this reason, to cultivate the technical feasibility and perspectives of the nano structure graphite matter was needed exceeding the knowledge of the structure acquired until now or the manufacture approach.
[0005]
[Means for Solving the Problem] Invention of this application is made in view of the technical-problem situation as above, and offers the approach for the new nano structure graphite matter and its manufacture. That is, first, invention of this application is the monolayer of the thickness equivalent to the magnitude of a carbon atom, and provides the 1st with the monolayer carbon nano horn structure characterized by constituting the structure of an air cone configuration.
[0006] And invention of this application provides the 2nd with the monolayer carbon nano horn structure whose radius of curvature of the closeout point of a cone configuration is 4nm or less the 3rd about the monolayer carbon nano horn structure whose magnitude of the path to which the shaft-orientations die length of a cone configuration is 60nm or less, and intersects perpendicularly with shaft orientations is 6nm or less about said structure. Moreover, invention of this application is a spherical particle to which said structures of either the 1st thru/or the 3rd either have gathered, and provides the 4th with the monolayer carbon nano horn structure whose magnitude of a spherical particle is 120nm or less the 5th about the monolayer carbon nano horn structure characterized by the closeout point of cone

configuration structure going to the method of outside from the core of a spherical particle.
[0007] Invention of this application also offers the monolayer carbon nano horn structure characterized by being the structure to which said spherical particles of either the 4th or a 5th have gathered further again. In the above new quality of the nano structure, in addition, invention of this application It is the manufacture approach of said monolayer carbon nano horn structure of either the 4th or a 5th, and the solid-state-like carbon simple substance matter is received the 7th. In an inert gas ambient atmosphere The manufacture approach of the monolayer carbon nano horn structure characterized by collecting the spherical particles to which irradiated the laser beam, and carry out carbon laser evaporation, the solvent was made to suspend and distribute the obtained soot-like matter, and a single or plurality subsequently gathered, It is the manufacture approach of said 6th monolayer carbon nano horn structure, and the solid-state-like carbon simple substance matter is received the 8th. In an inert gas ambient atmosphere A laser beam is irradiated, carbon laser evaporation is carried out and the manufacture approach of the monolayer carbon nano horn structure characterized by obtaining the structure to which spherical particles gathered as soot-like matter is offered.
[0008] Furthermore, invention of this application provides the 9th also with the manufacture approach of the monolayer carbon nano horn structure which expanded contacting said structure of either the 1st thru/or the 6th either to an oxidizing substance, and expanding the path of the closeout point of a cone configuration, and the diameter of a point characterized for a closeout point by open Lycium chinense.
[0009]
[Embodiment of the Invention] Although invention of this application has the description as above, if it explains further, said the 1st thru/or monolayer carbon nano horn structure as the 3rd invention has new nano graphite structure, and it is fundamentally different from well-known fullerene and a well-known carbon nanotube conventionally.
[0010] The monolayer carbon nano horn structure of this invention is matter which is extremely characteristic as what has the shape of an air cone which the diameter of a tube increases continuously, i.e., angle (horn)-like structure, rather than has a fixed diameter of a tube like a carbon nanotube. Of course, it is not strictly limited to the thing of a geometric definition with "the shape of a cone said here." It is a cone-like, the shape of i.e., an angle (horn), as an outline also including this thing. That description For example, as typically shown in drawing 1 , it sets in the whole structure also including a bent thing and a thing without that right. A part of [ at least ] structures make a closeout point (1) top-most vertices, and it is specified as structure which the path (D) of the tube (tubing) configuration section (2) is increasing continuously. And a closeout point (1) and the tube (tubing) configuration section (2) are formed by each as monolayer structure of the thickness equivalent to the magnitude of one carbon atom in that case.
[0011] Moreover, the monolayer carbon nano horn structures of these cone configuration will gather, and it being characteristic in this invention will be that the closeout point of a cone configuration exists as a spherical particle located toward the method of outside from the core, if that existence mode illustrates typically the monolayer carbon nano horn structure of the above cone configuration. For example, actually, if it explains as a transmission electron microscope (TEM) photograph, drawing 2 shows the case where the spherical particle of this aforementioned invention is in a state of aggregation. As for each spherical particle, the path (diameter) has typically 120nm or less of magnitude of ten to 100 nm. Drawing 3 is the TEM photograph expanded and shown about this spherical particle. Moreover, drawing 4 is the TEM photograph in which the front face of a spherical particle was further expanded, and was shown.
[0012] A spherical particle consists of an angle (horn)-like, i.e., conoid, set, and each angle (horn)-like object has the structure to which the closeout point projected from the core of a spherical particle to the radial toward the method of outside so that clearly from the photograph of drawing 3 . If it puts in another way, the spherical particle has the structure similar to the flower of the dahlia in which a point has the cauloid petal of a cone form, or the flower of a chrysanthemum of a certain kind.
[0013] And it is not cylindrical and it turns out that a point [ like the conventional carbon nanotube ] whose angle (horn)-like object from the photograph of drawing 4 is and which projected on the particle

front face of this tubing in the configuration near tubing of a cone form is closed. In addition, since another edge is located in the interior of the core region of a spherical particle, the edge structure is not shown clearly. For example, the angle (horn)-like object is constituted by the monolayer graphite of the thickness equivalent to the magnitude of one carbon atom, and has the cone configuration as the tubular structure which the end closed as shown in the above drawing 3 and drawing 4 .

[0014] For example, the 50nm or less of the shaft-orientations die length of the cone configuration which projected on the spherical particle front face in this case is ten to 30 nm more typically, 6nm or less of magnitude of the aforementioned path (D) which intersects perpendicularly with shaft orientations is 4nm or less typically, and 4nm or less of radius of curvatures of the closeout point of a cone configuration is one to 3 nm typically. The aspect ratio of the aforementioned path (diameter) and shaft-orientations die length is smaller than the usual monolayer carbon nanotube known conventionally.

[0015] The monolayer carbon nano horn structure as invention of this application is first made into the structure which makes that part the angle (horn)-like object of the cone configuration as above at least the 1st. And these structures shall gather in the 2nd as one existence mode, and the spherical particle as aforementioned shall be formed in it. By this invention, the matter in the condition that the aforementioned spherical particles have gathered is also offered further again. As for this condition, that mode is illustrated as matter of the TEM photograph of drawing 2 . It more specifically exists as soot-like matter. That is, they are black fine particles.

[0016] The monolayer carbon nano horn structure by this invention as above is the new matter which cannot be manufactured depending on the approach learned conventionally, and its manufacture approach is also completely new. As the manufacture approach, the following approach is offered in this invention.

To the <A> solid-state-like carbon simple substance matter, in an inert gas ambient atmosphere, a laser beam is irradiated, carbon laser evaporation is carried out and the fine particles to which spherical matter gathered are obtained as the aforementioned soot-like matter.

<B> Said spherical particles in the condition that suspended the fine particles as obtained soot-like matter in the solvent further, and a single or plurality gathered are collected.

[0017] as the mode of more desirable operation -- carbon laser evaporation -- reactions including rare gas, such as Ar (argon) and helium (helium), -- the inside of an inactive gas ambient atmosphere -- setting -- high power CO 2 Laser beams, such as gas laser light, are irradiated at a suitable include angle to the front face of the solid-state-like carbon simple substance matter, and are performed. As an output of a laser beam, it is more than 20W, and pulse width is 20 - 500ms, and considers as the thing of continuous oscillation preferably. The range of whenever [ illuminating-angle ] is 120 - 140 degrees more preferably 100 to 170 degrees as an include angle of the aforementioned solid matter front face and an exposure laser beam. Moreover, the container with which carbon laser evaporation is performed is preferably evacuated to 10 - 2 or less Pa, and is made into the ambient atmosphere conditions of 103 - 105 Pa with inert gas, such as Ar.

[0018] About the diameter of a spot on the front face of solid matter of the laser beam at the time of an exposure, it is about 0.5-5mm, for example. Moreover, as carbon simple substance matter as solid matter, round bar-like sintering carbon, compression-molding carbon, etc. can be used, for example. It deposits on a suitable substrate, and can collect and soot-like matter can be collected by the approach of the particle recovery with a dust bag. Inert gas is circulated within a reaction container and collecting these soot-like matter by the flow of inert gas is taken into consideration.

[0019] Subsequently, the obtained soot-like matter can be made into the spherical particle in the condition that a single or plurality gathered. In this case, a kind of various kinds of organic solvents, such as aliphatic hydrocarbon, such as aromatic hydrocarbon, such as various alcohols, benzene, and toluene, and a hexane, a heptane, halogenated hydrocarbon, the ether, and an amide, or two sorts or more of mixture can be used as a solvent.

[0020] It will suspend in a solvent and said spherical particles of two or more states of aggregation can be individually collected performing ultrasonic stirring, a decantation, etc. and by repeating as occasion

demands. In the manufacture approach of this invention as above, there is no need of carrying out simultaneous evaporation of a metal like Fe, nickel, and Co as a catalyst, like a conventional method.
[0021] An approach with the following descriptions is also offered by this invention further again. That is, it is with open Lycium chinense about a closeout point at contacting the monolayer carbon nano horn structure of the aforementioned cone configuration to an oxidizing substance, and expanding the path of the closeout point of a cone configuration, and a pan. Drawing 5 is the TEM photograph which illustrated this structure where it was expanded and the closeout point was opened.
[0022] A gas or liquefied any are sufficient as the oxidizing substance in this case, for example, matter, such as oxygen, and ozone, a carbon monoxide, a hydrogen peroxide, is illustrated. It is also effective in atmospheric air to heat in temperature of 200-400 degrees C. Although it will emphasize again, the monolayer carbon nano horn by this invention is the new matter uncompoundable in a conventional method, and its synthetic approach is also completely new. Therefore, the technique of competing does not exist. Although the carbon nanotube and the nano capsule are known as matter near the new matter of this invention, a big difference is in structure or a gestalt, therefore those properties and applications expected also differ from each other. Moreover, as other allied substances, although activated carbon and an activated carbon fiber exist, the atomic arrangement structure of those matter differs from the monolayer carbon nano horn by this invention fundamentally, and chemical differs also from a physical characteristic. Since the structure and the gestalt which contain atomic arrangement compared with activated carbon etc. can evaluate the matter by this invention by atomic level, a design more concrete than the case where industrial application is considered, and precise is attained. Moreover, prediction of an activity result is also possible.
[0023] Since the monolayer carbon nano horn by this invention is graphite structure fundamentally, that application crosses the chemical industry to activated carbon with an application extensive as a subject, a carbon fiber, an activated carbon fiber, and the extensive field for which fullerene and a carbon nanotube are used further. It is as follows when it classifies according to the description of the monolayer carbon nano horn structure and its field of the invention.
[0024] 1) The monolayer carbon nano horn structure is obtained as black fine particles.
2) This thing is fine particles with the pore of nano meter size.
3) 120nm or less of fine particles of diameters is the aggregate of the particle of ten to 100 nm typically.
4) The particle front face is covered by the projection of nano meter size.
[0025] 5) It is the corniform structure which the projection of nano meter size consisted of graphite-like carbon film of a monolayer, and the head closed, and, typically, 6nm or less of the average diameter is two to 4 nm.
6) Open Lycium chinense grows in the head of a projection of nano meter size easily in oxidation reaction.
7) It has a very big specific surface area.
[0026] 8) Excel in gas absorption and occlusion.
9) Absorb a metal easily and form an intercalation.
10) There is capillarity.
11) It will be in a colloidal state easily and becomes a particulate material.
12) It is easy to make it a thin film.
13) It is very stable chemically and thermally.
14) electric -- it is a conductor.
15) Excel mechanically.
16) Neither amorphous carbon nor other carbon structures are intermingled.
17) The mixture thing of an impurity metallurgy group is not included at all.
18) It becomes water repellence by fluorine processing.
19) A consistency is very small and is a charge of super-lighter weight materials.
20) Excel in heat absorption nature.
[0027] The application to the industry which harnessed such a description can be given to below. To the 1st, the application to high-tech industry, such as a gas adsorption ingredient, a catalyst support

ingredient, etc. which make representation a lithium ion battery electrode material and a hydrogen absorption ingredient, the chemical industry, and an environmental problem can be first considered in the field for which activated carbon is used.
[0028] In the field which uses that specific surface area is large for the 2nd, the utilization as an electric capacitor is also considered by the application to medicine, and the pan as a 'nano capsule' which makes drugs stick to a particle front face except activated carbon relation. The charge of lubricant is mentioned to the application which harnessed the description as a spherical particle and super-low consistency matter in the 3rd.
[0029] The nano size cornu on the front face of a spherical particle can be used for the 4th as a probe of STM or AMF. Moreover, a particle is applied to a conductive substrate and it is used as a cold cathode electron source by preparing a counterelectrode in a substrate and impressing an electrical potential difference to it. In the 5th, an aperture and its part can be chemically embellished with oxidation reaction etc. for a part for the point of the generated monolayer carbon nano horn, and composite material can be invented in it.
[0030] Hereafter, an example is shown and it explains in more detail. Of course, this invention is not limited to the following examples.
[0031]
[Example] (Example 1) After installing the sintering round bar-like carbon as solid-state-like carbon simple substance matter in the vacuum housing and evacuating the inside of a container even to ten to 2 Pa, Ar (argon) gas was introduced so that it might become the ambient pressure of 6x104 Pa.
[0032] Subsequently, CO2 of high power The include angle with the front face of the carbon simple substance matter to make was irradiated in gas laser light (output 100W, 20ms of pulse width, continuous oscillation) as 120 degrees. Carbon laser evaporation was performed by this and the soot-like matter was generated. It is drawing 2 - drawing 4 which showed the result of having observed the collected soot-like matter with the transmission electron microscope (TEM).
[0033] Drawing 2 shows that soot-like matter is fine particles with a diameter of 10-100nm which consist of a set of a spherical particle mostly. Each spherical particle from the enlarged drawing of drawing 3 is the aggregate of an angle (horn)-like body with a diameter [ of the air section ] of 1-4nm, and it turns out that an angle (horn)-like body is formed in a radial from the core of a spherical particle, and it has the structure which projected in the surface section. And the amount of [ which the angle (horn)-like matter has a cone configuration from the enlarged drawing having shown the front face of the spherical particle of drawing 4 , and projected on the surface of the spherical particle ] point is the closed structure, and it turns out that the radius of curvature is one to 3 nm.
[0034] The corniform body of a cone configuration consists of monolayer graphite of the thickness equivalent to the magnitude of a carbon atom piece, and the centrum diameter of the die length is one to 4 nm as mentioned above in 20-50nm or less extent.
(Example 2) The soot-like matter manufactured in the example 1 was suspended in the ethanol as a solvent, and ultrasonic stirring (the frequency of 40kHz, time amount 60 minutes) and a decantation were repeated 4 times.
[0035] Thereby, the spherical particle seen in the example 1 was able to be obtained as what consists of an isolated particle and some particles.
(Example 3) The aggregate of the spherical particle manufactured in the example 1 was heated in dry air in the temperature of 380 degrees C for 3 hours.
[0036] It is the TEM photograph in which the front face of the particle after heating was shown, and, as for drawing 5 , it turns out that the monolayer carbon nano horn structure which the closeout point of a cone configuration expanded is obtained. Moreover, the closeout point of some cone configurations is opened.
[0037]
[Effect of the Invention] The new nano graphite structure from which the development as new functional material is expected is offered by invention of this application as explained in detail above. Moreover, the simple manufacture approach for it is also offered.

---

[Translation done.]

* NOTICES *



1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

---

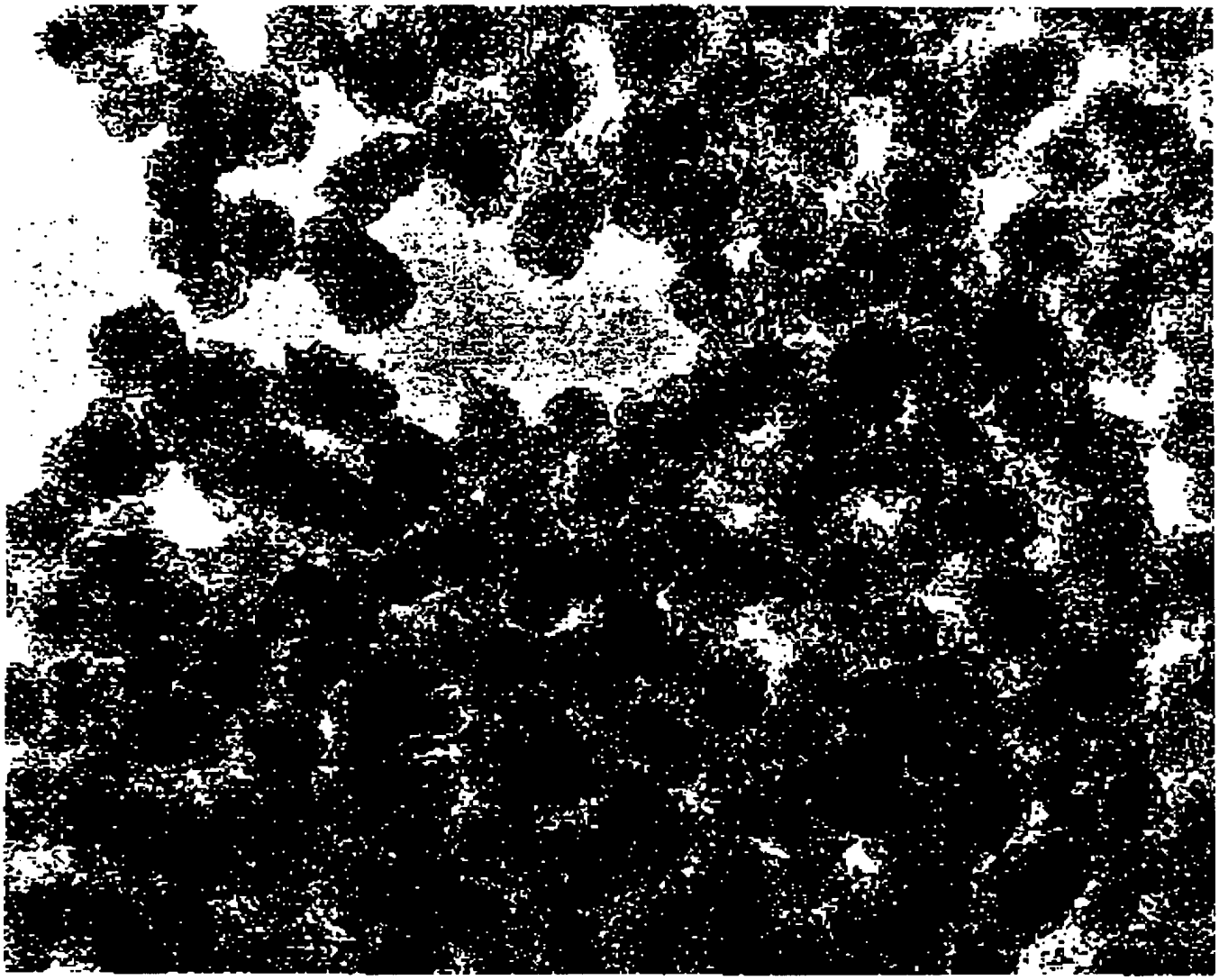
CLAIMS

---

[Claim(s)]
[Claim 1] The monolayer carbon nano horn structure characterized by constituting the structure of an air cone configuration from a monolayer of the thickness equivalent to the magnitude of a carbon atom.
[Claim 2] The monolayer carbon nano horn structure of claim 1 whose magnitude of the path to which shaft orientations and the shaft-orientations die length of a cone configuration cross at right angles by 60nm or less is 6nm or less.
[Claim 3] The monolayer carbon nano horn structure of claims 1 or 2 whose radius of curvatures of the closeout point of a cone configuration are 4nm or less.
[Claim 4] The monolayer carbon nano horn structure which is the spherical particle to which the structures of claim 1 thru/or either of 3 have gathered, and is characterized by the closeout point of cone configuration structure going to the method of outside from the core of a spherical particle.
[Claim 5] The monolayer carbon nano horn structure of claim 4 whose magnitude of a spherical particle is 120nm or less.
[Claim 6] The monolayer carbon nano horn structure characterized by being the structure to which one spherical particles of claims 4 or 5 have gathered.
[Claim 7] The manufacture approach of the monolayer carbon nano horn structure which is the manufacture approach of one monolayer carbon nano horn structure of claims 4 or 5, irradiates a laser beam and is characterize by collect the spherical particles to which carried out carbon laser evaporation, the solvent was made to suspend and distribute the obtained soot-like matter, and a single or plurality subsequently gathered in an inert gas ambient atmosphere to the solid-state-like carbon simple substance matter.
[Claim 8] The manufacture approach of the monolayer carbon nano horn structure which is the manufacture approach of the monolayer carbon nano horn structure of claim 6, and irradiates a laser beam, and carbon laser evaporation is carried out and is characterized by obtaining the structure to which spherical particles gathered as soot-like matter in an inert gas ambient atmosphere to the solid-state-like carbon simple substance matter.
[Claim 9] Contacting the structure of claim 1 thru/or either of 6 to an oxidizing substance, and expanding the path of the closeout point of a cone configuration, and the manufacture approach of the monolayer carbon nano horn structure which expanded the diameter of a point characterized for a closeout point by open Lycium chinense.

---

[Translation done.]


100nm

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

## BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☑ BLACK BORDERS
- ☑ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☑ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☑ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☑ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

**IMAGES ARE BEST AVAILABLE COPY.**
**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**